



## Short communication

## The application of a non-aqueous bis(acetylacetone)ethylenediamine cobalt electrolyte in redox flow battery

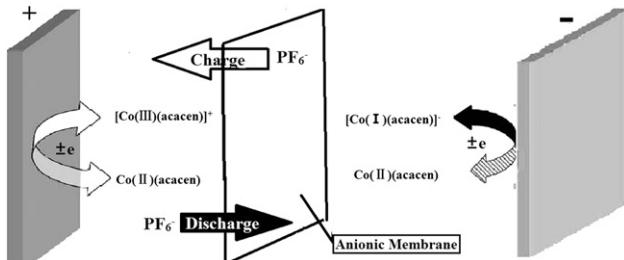
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## HIGHLIGHTS

- Co(acacen) was synthesized and evaluated in a non-aqueous redox flow battery.
- Cell potential for one-electron disproportionation was 2.0 V.
- Charge–discharge performance shows a good coulombic efficiency.
- The effect of the environmental factors has been evaluated.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 4 June 2012

Accepted 8 June 2012

Available online 16 June 2012

## Keywords:

Redox flow battery  
Bis(acetylacetone)ethylenediamine  
cobalt(II)  
Tetrabutylammonium hexafluorophosphate  
Non-aqueous electrolyte  
Energy storage

## ABSTRACT

A single-metal redox flow battery employing bis(acetylacetone)ethylenediamine cobalt(II) as the active species and tetrabutylammonium hexafluorophosphate as the supporting electrolyte with acetonitrile as the solvent has been examined. Cyclic voltammetry is used to measure the electrode kinetics of the anodic and cathodic reactions. Three redox couples are observed in the stable potential window, these electrode reactions are quasi-reversible and together yield a cell potential of 2.0 V. The disproportion reactions of active species are controlled by the diffusion coefficient. The effect of the environmental factors, such as temperature, oxygen and water, has been tested in the experiment. The charge–discharge characteristics of this system are evaluated in an H-type glass cell. The coulombic efficiencies 90.24% and 87.88% in cycle 5 and cycle 8 are obtained, respectively, with 1 mA charge 0.5 mA discharge current.

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## 1. Introduction

Energy is an indispensable element in our everyday life. However, approximately 80% of the present world energy consumed comes from fossil fuels [1]. Solar, wind, and biomass are promising renewable energy resources but they are generally site-specific, intermittent, and thus, not stable. For a stable supply from the renewable energy resources, large- and medium-scale energy storage technologies are of great importance. A redox flow battery

(RFB) is a kind of promising large-scale energy storage device which utilizes oxidation and reduction reactions of two redox couples in the electrolytes for charge and discharge.

A number of RFBs classified by different active species have been developed, such as iron–chromium [2,3], all vanadium [4–6], bromine–polysulfide [7], and zinc/bromine [8,9] RFBs. Generally, most of the RFBs examined in literature employ aqueous phase electrolyte. Therefore, the operating potential of them is constrained by the electrochemical potential window of water (depending on pH, generally lower than 2.0 V) [10]. Organic solvents offer a much higher potential window, e.g. 5.0 V for acetonitrile ( $\text{CH}_3\text{CN}$ ), with which, much higher power and energy output can be obtained [11–16].

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Chakrabarti et al. [11] evaluated ruthenium acetylacetone  $[\text{Ru}(\text{acac})_3]$  and tris(2,2-bipyridine) iron(II) perchlorate  $[\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2]$  in non-aqueous redox flow batteries. The open circuit voltages are 1.8 V and 2.41 V, respectively, and are both much higher than that of all vanadium RFBs with aqueous electrolytes. However, the large-scale application of electrolytes is limited by the too high cost of ruthenium and 2,2-bipyridine. Recently, Liu [13] studied vanadium acetylacetone  $[\text{V}(\text{acac})_3]$  and a cell potential of 2.1 V is obtained, but the active species can be easily deteriorated in the presence of impurities and the energy density is limited by the low solubility of  $\text{V}(\text{acac})_3$  in  $\text{CH}_3\text{CN}$ .

As mentioned above, the organic metal complexes used in non-aqueous RFB systems mainly fall into two sorts, the acetylacetone complexes and the 2,2-bipyridine complexes. In this work, the third kind complexes, bis(acetylacetone)ethylenediamine complexes, is employed. Bis(acetylacetone)ethylenediamine cobalt(II)  $[\text{Co}(\text{acacen})]$  and tetrabutylammonium hexafluorophosphate ( $\text{TEAPF}_6$ ) were synthesized and used in the non-aqueous system as active species and supporting electrolyte, respectively. The potential application of  $\text{Co}(\text{acacen})$  in non-aqueous RFBs was evaluated using cyclic voltammograms and the charge–discharge performance was determined using a static H-type cell.

## 2. Experimental

### 2.1. Electrolytes

$\text{Co}(\text{acacen})$  was synthesized before the experiments. Firstly Schiff base was prepared with the reaction of pure ethylenediamine and acetylacetone at 60 °C for 4 h [16], recrystallized in water and vacuum-dried. For the preparation of the cobalt(II) complexe,  $\text{Co}(\text{OH})_2$  was mixed with the Schiff base and refluxed at 70 °C for 9 h in  $\text{CH}_3\text{CN}$ . With the cooling of the reaction mixture, water was added to recrystallize the crystallites at 0 °C. At last the product was dried in vacuum at 40 °C for 24 h. The IR spectra of the prepared complexe were recorded for the presence of functional groups and coordination sites of the Schiff base.

The electrolytes were prepared with dissolving  $\text{Co}(\text{acacen})$  and  $\text{TEAPF}_6$  in anhydrous  $\text{CH}_3\text{CN}$  (Guangfu, China).  $\text{TEAPF}_6$  was synthesized as described in the literature [17] and used as supporting electrolyte for the RFB.

### 2.2. Cyclic voltammetry

Cyclic voltammetry was performed using a Versa STAT 3 electrochemistry work station (Princeton Applied Research, U.A.). A three-electrode cell was used with a glassy carbon electrode (Aidahengsheng, China) with  $0.28 \text{ cm}^2$  surface area as working electrode, a graphite plate (Aidahengsheng, China) as the counter electrode and a silver/silver ion ( $\text{Ag}/\text{Ag}^+$  with  $\text{CH}_3\text{CN}$  as solvent) electrode (Aidahengsheng, China) as the reference electrode which was connected to the working electrode via a Luggin capillary. The working electrode was polished with 1200 grit silicon carbide polishing paper, ultrasonically cleaned with deionized water and dried at 80 °C for 24 h [13].

Prior to the experiments, the electrolyte was deoxygenated by bubbling with dry nitrogen (Liufang, China) for at least 30 min. For experiments involving oxygen, solutions were subsequently oxygenated with oxygen gas (Liufang, China). All the experiments were performed at atmospheric pressure.

### 2.3. Charge–discharge experiments

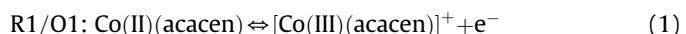
Charge–discharge tests were performed in an H-type glass cell with each electrolyte compartment containing 15 ml electrolyte

and a magnetic stirrer. Graphite electrodes with a dimension of  $80 \text{ mm} \times 15 \text{ mm} \times 5 \text{ mm}$  were employed as both the anode and cathode. An Ultrex™ AMI-7001 (Membranes International Ltd., U.S.) anion-exchange membrane with a diameter of 35 mm is used as the separator. Prior to the test, the membrane was pre-treated by soaking it into the test solution for more than 4 h. Galvanostatic method was used with charge and discharge current being 1 mA and 0.5 mA, respectively. The cell was charged up to a potential of 2.1 V and the discharge cutoff voltage was set as 0 V. The test was performed under atmospheric pressure with bubbling nitrogen.

## 3. Results and discussion

### 3.1. Cyclic voltammograms and kinetic behavior of electrode reactions

Fig. 1 shows the cyclic voltammograms for  $0.01 \text{ mol l}^{-1} \text{ Co}(\text{acacen})$  and  $0.1 \text{ mol l}^{-1} \text{ TEAPF}_6$  in  $\text{CH}_3\text{CN}$  during the initial 50 cycles recorded with a scan rate of  $0.50 \text{ V s}^{-1}$ . As described in literature [17],  $\text{TEAPF}_6$  can be regarded as electrochemically inert within the solvent stable window ( $-2.5$ – $0$  V vs.  $\text{Ag}/\text{Ag}^+$ ). The three redox couples observed in the experiment can be attributed to the reactions of the active species in the electrolyte. According to the work of Boltzcher et al. [18], the first two current peaks were attributed to the following reactions:



While, there is also a third current peak couple R3/O3 existed at  $-2.3$  V (vs.  $\text{Ag}/\text{Ag}^+$ ).

Richert et al. [19] reported the electrochemical behavior of  $[\text{Co}(\text{bpy})_3(\text{ClO}_4)_2]$  in  $\text{CH}_3\text{CN}$  and also observed two reduction couples. The second reduction peak observed at very negative potential was attributed to the reduction of  $\text{Co}(\text{I})$ . Similarly, the third redox current peak couple, R3/O3, is consequently attributed to the following reaction:



The formal potential of each half reaction was estimated by taking the average of the anodic and cathodic peak potentials from

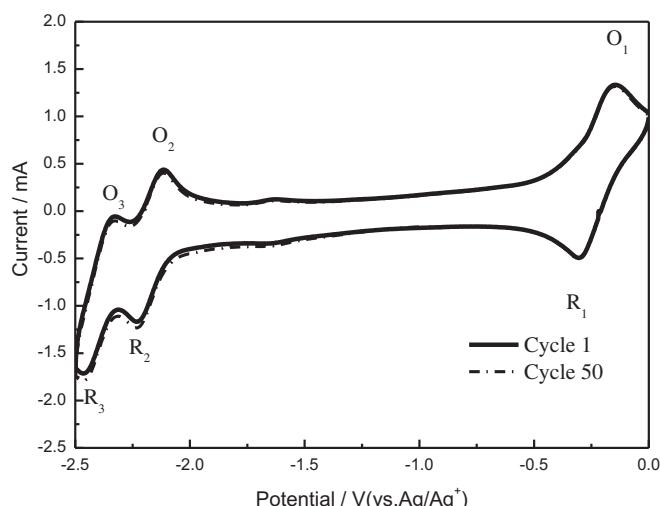


Fig. 1. Cyclic voltammograms in  $0.01 \text{ mol l}^{-1} \text{ Co}(\text{acacen})$  and  $0.1 \text{ mol l}^{-1} \text{ TEAPF}_6$  in  $\text{CH}_3\text{CN}$  at 25 °C with a scan rate of  $0.50 \text{ V s}^{-1}$ .

the cyclic voltammogram. For electrode reaction Co(III)/Co(II), The formal potential is  $-2.2$  V, that is  $-0.2$  V for the reaction Co(II)/Co(I). From these formal potentials, the cell potential for the Co(acacen) system is  $2.0$  V, which is approximately  $60\%$  higher than the potential for conventional aqueous vanadium system [20]. Compared the first and the fiftieth cycle, almost no variation is observed among the recorded voltammograms. This suggests that the cycling stability and the reversibility of Co(acacen) are electrochemically favorable. The cyclic voltammograms show that Co(acacen) as an active species is suitable for the non-aqueous RFB application.

A series of cyclic voltammograms with different scan rates from  $0.10$  to  $0.80$   $V s^{-1}$  for an electrolyte containing  $0.01$  mol  $l^{-1}$  Co(acacen) and  $0.1$  mol  $l^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN are plotted in Fig. 2. No obviously change is observed in the profile of cyclic voltammograms but the peak potential separations increased gradually with the increase of the scan rate. For the Co(II)/Co(I) redox couple, the peak separation ( $\Delta E_p$ ) increased from  $89$  to  $133$  mV as the scan rate increased from  $0.05$  to  $0.50$   $V s^{-1}$ . Similarly, for the Co(III)/Co(II) redox couple,  $\Delta E_p$  increased from  $123$  to  $183$  mV as the scan rate increased. Here it can be concluded that both reactions (1) and (2) are quasi-reversible in the acetonitrile.

A plot of the peak currents for Co(II) disproportion reaction as a function of the square root of the scan rate is presented in Fig. 3. For both the reduction process of Co(II) to Co(I) and the oxidation of Co(II) to Co(III), a linear response is obtained, indicating the fast electrode kinetics for the Co(II) disproportion reaction and the diffusion controlled nature of the reaction. The diffusion coefficients of Co(acacen) based on the slope of the straight line can be estimated to be in the range of  $4.33\text{--}6.98 \times 10^{-6}$   $cm^2 s^{-1}$ .

### 3.2. Influence of the operating factors

Cyclic voltammograms in  $0.01$  mol  $l^{-1}$  Co(acacen) and  $0.1$  mol  $l^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN at various temperatures are shown in Fig. 4. The reversibility of Co(acacen) did not show a significant change in the temperature range from  $0$  °C to  $50$  °C, which means Co(acacen) can be used in the non-aqueous RFB as active species at a broad range of temperature. For traditional aqueous systems, the operating temperature is limited to above  $0$  °C, but it is not for non-aqueous system, that is an important advantage in the application.

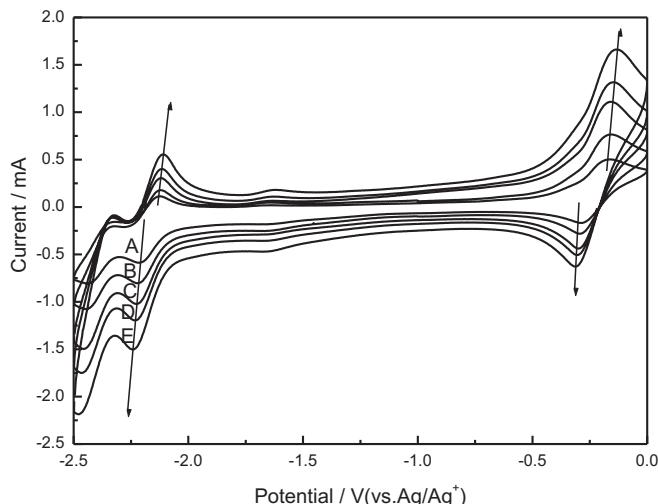


Fig. 2. Cyclic voltammograms in  $0.01$  mol  $l^{-1}$  Co(acacen) and  $0.1$  mol  $l^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN at  $25$  °C with different scan rates: (A)  $0.10$  (B)  $0.20$  (C)  $0.35$  (D)  $0.50$  (E)  $0.80$   $V s^{-1}$ .

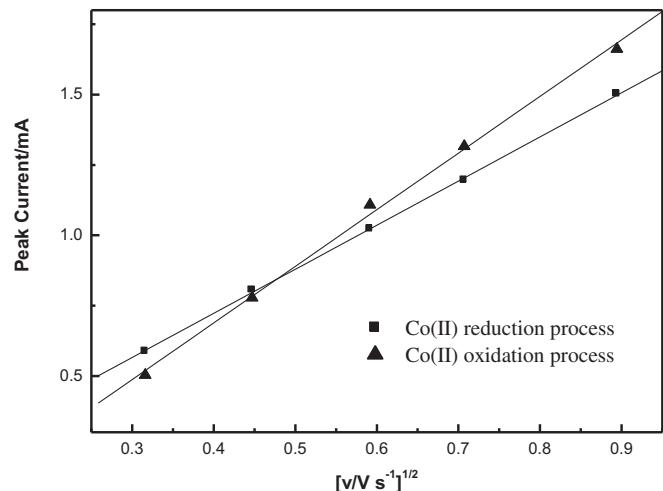


Fig. 3. Plots of the peak current for Co(II) disproportion reaction versus the square root of scan rate.

It was found that the effect of the temperature mainly concerns such points: (1) the peak currents for the two redox couples increase with the increase of temperatures, which is probably caused by the increased diffusion coefficients of the active species. In the cyclic voltammogram, the peak current is proportional to the diffusion coefficient, so with a higher temperature, a higher peak current is obtained. (2) For the Co(II)/Co(I) redox couple, no obviously change in peak separation is observed. However, for the Co(III)/Co(II) redox couple, peak separation decreased clearly when the temperature increased from  $0$  °C to  $25$  °C, which mainly results from the shift of the cathodic peak to the positive direction. (3) The ratio of the anodic to cathodic peak current for the two redox couples is both far from unity, indicating the complexity in the electrode process.

Fig. 5 compares the cyclic voltammograms of oxygenated solution of  $0.01$  mol  $l^{-1}$  Co(acacen) and  $0.1$  mol  $l^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN with the deoxygenated solution at the ambient temperature. The oxygenated solution was oxygenated by bubbling with oxygen gas for  $1$  min. After the solution was oxygenated, the cyclic

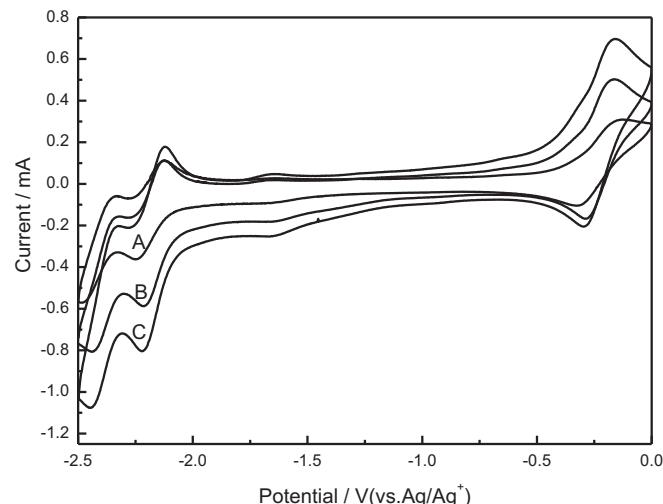
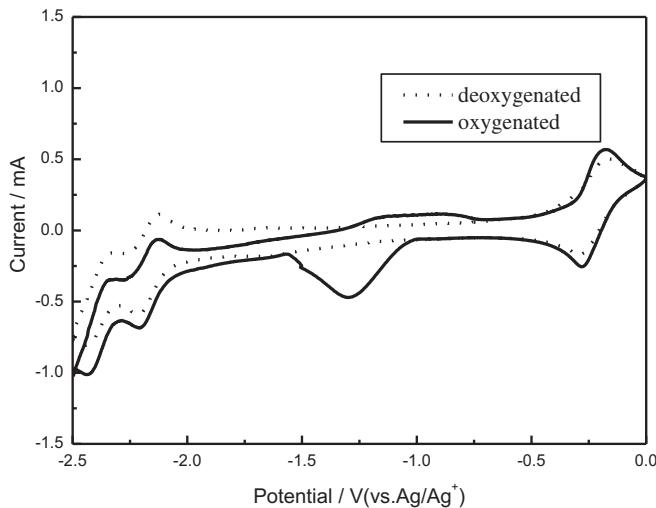


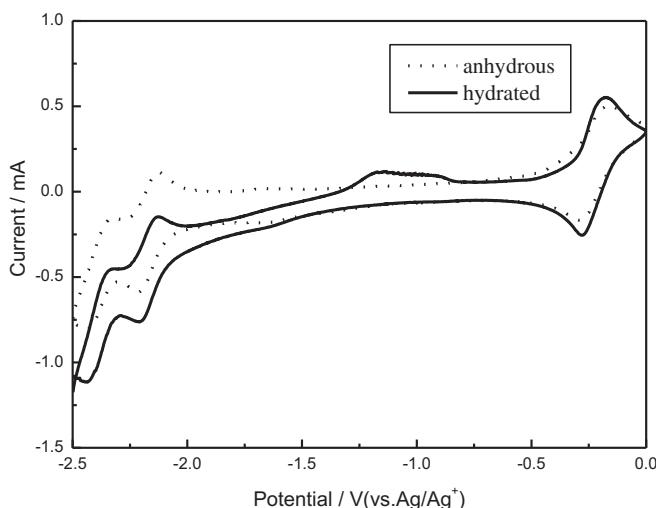
Fig. 4. Cyclic voltammograms in  $0.01$  mol  $l^{-1}$  Co(acacen) and  $0.1$  mol  $l^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN with a scan rates of  $0.10$   $V s^{-1}$  at various temperatures: (A)  $0$  °C (B)  $25$  °C (C)  $50$  °C.



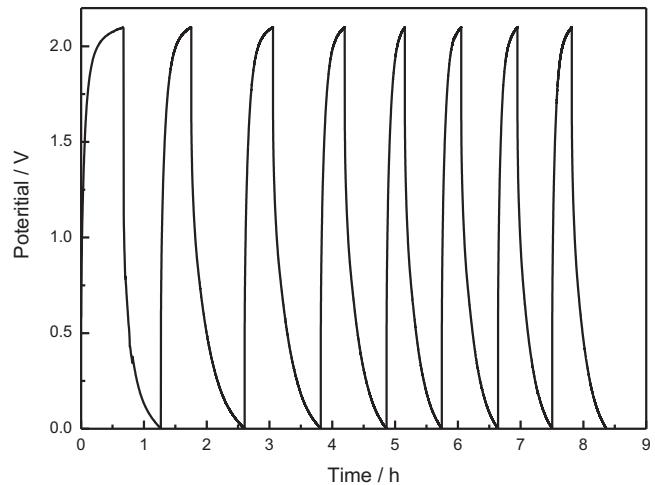
**Fig. 5.** Cyclic voltammograms in deoxygenated and oxygenated solutions of  $0.01 \text{ mol l}^{-1}$  Co(acacen) and  $0.1 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN at  $25^\circ\text{C}$  with a scan rate of  $0.10 \text{ V s}^{-1}$ .

voltammogram changed obviously, a new redox couple at  $-1.2 \text{ vs. Ag/Ag}^+$  is observed and the anodic peak for Co(II)/Co(I) redox couple is almost disappeared. At the same time, for the Co(III)/Co(II) redox couple, the peak current and potential remain virtually unchanged. Then the oxygenated solution was deoxygenated with dry nitrogen, the original cyclic voltammogram was reproduced. It suggests that there is no irreversible reaction between active species and oxygen occurred. The new couple may be due to the redox electrochemical reactions of the soluble oxygen molecule in the solution.

The cyclic voltammograms in anhydrous and hydrated solutions of  $0.01 \text{ mol l}^{-1}$  Co(acacen) and  $0.1 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN are drawn in Fig. 6. To examine the influence of the water in the non-aqueous RFB system, the hydrated solution containing 0.5 vol% water was compared with the anhydrous solution. A small anodic peak at  $-1.2 \text{ vs. Ag/Ag}^+$  is observed and like the oxygenated solution, the peak current and potential for Co(III)/Co(II) redox couple are invariable and the anodic peak for Co(II)/Co(I) redox couple is suppressed, while the cathodic peak increases significantly



**Fig. 6.** Cyclic voltammograms in anhydrous and hydrated solutions of  $0.01 \text{ mol l}^{-1}$  Co(acacen) and  $0.1 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> in CH<sub>3</sub>CN at  $25^\circ\text{C}$  with a scan rate of  $0.10 \text{ V s}^{-1}$ .



**Fig. 7.** Charge-discharge curves of the electrolytes with  $0.01 \text{ mol l}^{-1}$  Co(acacen),  $0.1 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> and  $I_d = 0.5 \text{ mA}$ ,  $I_c = 1 \text{ mA}$ , at  $25^\circ\text{C}$ .

especially for the third redox couple. This is probably caused by the electrolysis of the water on the electrode in high negative potential. Both oxygen and water show a negative effect on the performance of the non-aqueous system, these effects should be avoided in the practical application.

### 3.3. Charge-discharge performance

The charge-discharge performances of the RFB with Co(acacen) used as the active species for non-aqueous RFBs were evaluated with an H-type glass cell. Due to the low concentration of the active species in the electrolyte and the existence of a large ohmic drop and polarization in the H-type cell, a low current density was employed with charging current  $I_c = 1 \text{ mA}$  and discharging current  $I_d = 0.5 \text{ mA}$ . The charge cutoff voltage was set as  $2.1 \text{ V}$ , slightly higher than the  $2.0 \text{ V}$  cell potential for the one-electron disproportionation of Co(acacen). This potential should prevent the irreversible reduction of Co(I) observed in the cyclic voltammograms. The discharge cutoff voltage was set as  $0 \text{ V}$  to allow the system to be fully discharged.

Fig. 7 illustrates the first eight charge-discharge cycles. The coulombic and energy efficiencies reached relatively constant values after 4 cycles, and then similar charge-discharge curves are observed. The discharge voltages are lower than the cell voltages achieved by cyclic voltammograms. This may be caused by the large ohmic drop and polarization in the H-type cell. The low conductivity of the electrolyte, the relatively large distance between the two electrodes and the presence of the separator probably lead to a large Ohm drop.

The coulombic efficiency is 90.24% and 87.88% in cycle 5 and cycle 8. The loss of the coulombic efficiency was possibly caused by the crossover of the active species through the anion-exchange membrane and/or unknown side reactions. Further investigation is needed to modify the membrane to fit the non-aqueous system.

## 4. Conclusions

A Schiff base complexes – bis(acetylacetone)ethylenediamine cobalt(II) was synthesized and evaluated in a non-aqueous acetonitrile redox flow battery as active species with tetrabutylammonium hexafluorophosphate as supporting electrolyte.

The cyclic voltammograms indicate that the Co(acacen) complex can be oxidized to  $[\text{Co}(\text{acacen})]^+$  and reduced to  $[\text{Co}(\text{acacen})]^-$  at

a glassy carbon electrode. The anodic and cathodic half-cell reactions appeared to be electrochemically quasi-reversible and the cell potential for one-electron disproportion was 2.0 V. The peak currents for Co(II) disproportion reaction is proportional to the square root of scan rates, these indicate that the fast electrode reactions are fast and the process is diffusion controlled.

The impacts of the environmental factors were examined in the experiment. Good reversibility of Co(acacen) is observed in the tested temperature range, from 0 °C to 50 °C. Both oxygen and water cause the degradation of the non-aqueous RFB system, so they should be eliminated before the experiment and practical application.

Charge-discharge characteristics were evaluated in an H-type glass cell using a membrane separator. The coulombic efficiency of the electrolyte containing 0.01 mol l<sup>-1</sup> and 0.1 mol l<sup>-1</sup> TEAPF<sub>6</sub> is measured as 90.24% and 87.88% in cycle 5 and cycle 8 respectively.

The energy density of redox flow batteries is limited by the cell potential, the concentration of the active species and the number of electrons transferred during discharge per mole of active redox ions. The non-aqueous Co(acacen) redox flow battery show a higher cell potential than conventional vanadium system. Further studies are being performed in an attempt to estimate the solubility of Co(acacen) in CH<sub>3</sub>CN.

## Acknowledgements

The financial support of NSF of China under contract numbers 21076150 and 21120102039 is gratefully acknowledged. The work has been also supported by the Program of Introducing Talents to

the University Disciplines under file number B06006, and the Program for Changjiang Scholars and Innovative Research Teams in Universities under file number IRT 0641.

## References

- [1] D. Das, T.N. Veziroglu, *Int. J. Hydrogen Energy* 26 (2001) 13.
- [2] N.H. Hagedom, L.H. Thaller, *J. Power Sources* 8 (1981) 227.
- [3] M. Bartolozzi, *J. Power Sources* 27 (1989) 219.
- [4] M. Skyllas-Kazacos, M. Rychick, R. Robins, US Patent 4,786,567 (1988).
- [5] E. Sum, M. Skyllas-Kazacos, *J. Power Sources* 15 (1985) 179.
- [6] E. Sum, M. Rychick, M. Skyllas-Kazacos, *J. Power Sources* 16 (1985) 85.
- [7] A. Price, S. Bartley, S. Male, G. Cooley, *Power Eng. J.* 13 (3) (1999) 122.
- [8] H.S. Lim, A.M. Lackner, R.C. Knechtli, *J. Electrochem. Soc.* 124 (1977) 1154.
- [9] P.C. Butler, P.A. Eidler, P.C. Grimes, S.E. Klassen, R.C. Miles (Chapter 37), in: D. Linden (Ed.), *Handbook of Batteries*, McGraw Hill, New York, 1994.
- [10] C.H. Bae, Ph.D. Thesis, University of Manchester, Institute of Science and Technology, UK, (2001).
- [11] M.H. Chakrabarti, R.A.W. Dryfe, E.P.L. Roberts, *Electrochim. Acta* 52 (2007) 2189.
- [12] Y. Matstuda, K. Tanaka, M. Okada, Y. Takasu, M. Morita, T. Mastsumura-Inoue, *J. Appl. Electrochem.* 18 (1988) 909.
- [13] Q.H. Liu, A.E.S. Sleightholme, A.A. Shinkle, Y.D. Li, L.T. Thompson, *Electrochim. Commun.* 11 (2009) 2312.
- [14] Q.H. Liu, A.A. Shinkle, Y.D. Li, C.W. Monroe, L.T. Thompson, A.E.S. Sleightholme, *Electrochim. Commun.* 12 (2010) 1634–1637.
- [15] A.E.S. Sleightholme, A.A. Shinkle, Q.H. Liu, Y.D. Li, C.W. Monroe, L.T. Thompson, *J. Power Sources* 196 (2011) 5742.
- [16] K.C. Gupta, H.K. Abdulkadir, S. Chand, *J. Appl. Polym. Sci.* 90 (2003) 1398.
- [17] D.P. Zhang, Q.H. Liu, X.S. Shi, Y.D. Li, *J. Power Sources* 203 (2012) 201.
- [18] A. Boittcher, T. Takeuchi, K.I. Hardcastle, T.J. Meade, H.B. Gray, *Inorg. Chem.* 36 (1997) 2498.
- [19] S.A. Richert, P.K.S. Tsang, D.T. Sawyer, *Inorg. Chem.* 28 (1989) 2471.
- [20] C. Ponce de Leon, A. Frias-Ferrer, J. Gonzalea-Garcia, D.A. Szanto, F.C. Walsh, *J. Power Sources* 160 (1) (2006) 716.